

Entropic phase separation of linked beads

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We study theoretically a model system of a transient network of microemulsion droplets connected by telechelic polymers and explain recent experimental findings. Despite the absence of any specific interactions between either the droplets or polymer chains, we predict that as the number of polymers per drop is increased, the system undergoes a first order phase separation into a dense, highly connected phase, in equilibrium with dilute droplets, decorated by polymer loops. The phase transition is purely entropic and is driven by the interplay between the translational entropy of the drops and the configurational entropy of the polymer connections between them. Because it is dominated by entropic effects, the phase separation mechanism of the system is extremely robust and does not depend on the particular physical realization of the network. The discussed model applies as well to other systems of polymer linked particle aggregates, such as nano-particles connected with DNA linkers.

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Introduction: Equilibrium or transient gels are network-forming systems, examples of which include surfactant solutions, gels of biological molecules or synthetic polymers [1, 2, 3, 4, 5, 6, 9, 10, 11, 12]. Understanding the phase behavior and structure of such systems is an active field of research [7, 13, 14, 15, 16, 17, 18, 19, 20], and has a wide range of practical applications [1, 2, 7, 10]. A particularly elegant experimental realization of a transient network has been reported in [21]. The system consists of oil-in-water microemulsion droplets (which we call either drops or beads) connected by telechelic polymers (see Fig. 1 b)); the latter have a hydrophilic backbone with a hydrophobic group at each chain end. Mixtures of telechelic polymers and emulsions have a wide range of technological applications, including paints, cosmetics and enhanced oil recovery. Precision control of the structural and rheological properties of materials is essential for achieving good performance. Such control is currently achieved using the telechelic additives, that form a transient network with controlled rheological and structural properties [21]. Apart from its high applicative interest, the telechelic-microemulsion mixtures serve as a model system for a general class of transient networks. The advantage of this particular system is that the parameters that control the thermodynamics and structure can be easily identified and independently controlled: the *concentration of possible nodes* (the droplets) and the *connectivity of the network* (the number of polymers per droplet). This is in contrast, for example, with binary mixtures of telechelics, where one cannot separately control the number of nodes, formed by the associating chain ends. A similar system of gold nano-particles connected by short DNA segments, has been of a considerable interest recently [7, 8]

Due to the high hydrophobic energy of the stickers ($\sim 10 - 20k_B T$), the chain ends are constrained to lie within the droplets, and the number of dangling ends outside the droplets is statistically insignificant. Nevertheless, the

polymer ends can detach from a droplet and switch between loop (with both ends inside the same droplet) and bridge (with the chain ends residing in different droplets) configurations when the droplets are close enough. Polymer ends can also be exchanged between the droplets during droplet collisions. Rheological experiments show that the stress relaxation times, which are related to the timescale for chain rearrangement between the droplets, are of the order of one second [21]. Thus, the timescales of the observation (days) are much larger than the time for the polymers to explore different connectivity configurations, and the system can be considered to be in equilibrium. Although the system is *athermal*, it has been found [21] that for high polymer to bead ratios, the system undergoes a first-order phase separation. Independently, a non-thermodynamic, structural transition was observed, where an infinite connected network is formed, as reflected in rheological measurements. The experimentally observed phase diagram is shown in Fig. 1 a).

In this Letter, we investigate theoretically the phase behavior and structure of this experimental system. We predict that as the average number of polymers per bead is increased, the system undergoes a first-order phase separation into a highly connected dense network that coexists with a dilute phase of disconnected beads, decorated with polymer loops. This explains the experimental results of Ref. [21] and predicts how the polymer properties control the phase behavior. The predicted phase separation has a *purely entropic origin*; there are no energetic interactions among the polymers or droplets. The phase separation occurs because the loss of the translational entropy of the droplets is overcompensated by the high configurational entropy of the polymer connections in the dense network. The analytical results are confirmed by Monte Carlo simulations that also predict the phase separation.

Analytical model: We first discuss the thermodynamic behavior of the system. A total of N beads and N_p

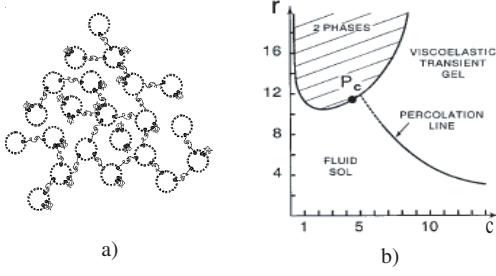


FIG. 1: a) Description of the connected microemulsion. The telechelic polymers can either link two oil droplets or loop on a single one. b) Experimentally observed phase behavior of the connected microemulsion as a function of the bead density c and the mean number of stickers per droplet, r .

polymers are distributed in space so that a polymer either connects two beads or loops on a single bead. The total free energy of the system, which in this athermal system amounts to the configurational entropy, includes two contributions. The first, is the translational entropy of the beads which we take as the lattice-gas entropy of mixing of a dispersion of hard spheres, $S_0(c) = -(c \ln c + (1-c) \ln(1-c))$, where c is the volume fraction of the beads and $S_0(c)$ is the entropy per site on the lattice. One should bear in mind that c is the effective volume fraction of the droplets, together with the tethered polymers. The experimentally controlled density of pure beads is roughly $c \frac{R_0^3}{(R_G + R_0)^3}$. The theory treating the effects of the excluded volume of the polymers, will be presented elsewhere. The second contribution to the free energy of the system is the configurational entropy of distributing the polymers among the beads. A polymer can either loop onto a single bead or bridge between two droplets. For a single polymer, there are $q_l N$ available looped states, where N is the number of the drops in the system and q_l is the number of positions available to a sticker of size a at the surface of a drop: $q_l \simeq \frac{4\pi R_0^2}{\pi a^2}$. A bridging polymer connecting two drops at a distance R , is stretched to a length R , with an entropic cost (in units of $k_B T$ and assuming ideal chains, for simplicity) $E_R \simeq \frac{3}{2} R^2 / R_G^2$ where R_G is the polymer radius of gyration. From simple geometric considerations, the average number of droplet pairs separated by a distance R is $\frac{1}{2} c N \frac{4\pi R^2}{R_0^2} g(R) \equiv q_R c N$ where R_0 is the radius of a drop and $g(R)$ is the normalized density-density correlation function of the drops. As a first step, in the mean field approximation we take $g(R) = 1$ for $R > R_0$. As we show later, the average number of looped polymers per bead is small. Thus, because there is no restriction on the number of polymers connecting two given drops (except at very high polymer concentrations, outside the range of the experiments), the polymers are independent. The partition function of a single polymer is

$Z_1 = q_l N e^{-\epsilon} + c N \sum_R q_R e^{-E_R/T}$ where ϵ is a free energy cost (in units of $k_B T$) of a looped polymer, that measures the entropic cost of both ends being confined to the same droplet. Taking into account the indistinguishability of the polymers, the configurational partition function of the total N_p polymers, that determines the polymer distribution among the beads is thus

$$Z_p = \frac{1}{N_p!} Z_1^{N_p} = \frac{(q_l c N + q_l e^{-\epsilon} N)^{N_p}}{N_p!} \quad (1)$$

where $q \equiv \int dR \frac{4\pi R^2}{\pi R_0^2} e^{-E_R/T}$, is the effective number of droplet pairs. It is determined by the balance of the Boltzmann factor for the stretching energy, that strongly decreases with distance, and the number of available positions, $\frac{4\pi R^2}{\pi R_0^2}$ that increases with distance R .

In the thermodynamic limit, where the number of drops, polymers and the number of lattice sites, V , all become infinite, the free energy per site (in units of $k_B T$), $f \equiv -\frac{1}{V} \ln Z_p - S_0(c)$ is

$$f = c \ln c + (1-c) \ln(1-c) + \phi (\ln \phi - 1) - \phi \ln(qc^2 + c q_l e^{-\epsilon}) \quad (2)$$

where $c = N/V$ and $\phi = N_p/V$ are the densities of the droplets and of the chains respectively. The first two terms account for the translational entropy of the droplets and the third term is the translational entropy of the polymer chains (the excluded volume of the polymers is neglected at this stage). The last term is the effective, entropically-induced attraction between the polymers and droplets; this term causes the free energy to decrease when the concentration of the beads or polymers/beads ratio is increased. We stress that there are no specific interactions between the droplets and/or the polymers, and the resulting thermodynamic attraction is of purely entropic origin. The system is thermodynamically stable if the free energy $f(\phi, c)$ (eq. (2)) is a convex function of both ϕ and c . Formally, this means that the second variation of the free energy, $\delta^2 F = F_{\phi\phi} \delta\phi^2 + F_{cc} \delta c^2 + 2F_{c\phi} \delta\phi \delta c$ is positive so that the stability matrix $\hat{S} \equiv \begin{bmatrix} F_{\phi\phi} & F_{c\phi} \\ F_{c\phi} & F_{cc} \end{bmatrix}$ is positive definite i.e. possessing two positive eigenvalues. Because $F_{\phi\phi} = \frac{1}{\phi}$ is always positive, it is sufficient for the determinant $\text{Det } \hat{S}$ to be positive, in order to guarantee convexity. Using Eq. (2) for $f(\phi, c)$, one finds $\text{Det } \hat{S} = -2 \frac{1}{c(c + \frac{q_l}{q} e^{-\epsilon})} + \frac{1}{\phi c(1-c)}$ and the system is thermodynamically stable only if

$$2\phi/c < \frac{c + \frac{q_l}{q} e^{-\epsilon}}{c(1-c)} \quad (3)$$

where $2\phi/c \equiv r$ is the average number of stickers (polymer chain ends) per droplet. This stability condition defines the spinodal line in the (c, r) plane as shown in Fig. 2. Note that because the destabilizing effect comes from the cross-terms, $F_{c\phi}$, the tie-lines are *not* horizontal, but

connect points with different values of r . If $r > \frac{c + \frac{q_l}{q}e^{-\epsilon}}{c(1-c)}$, the system is thermodynamically unstable and phase separates into a system of dense droplets that are highly connected by polymers, that coexists with a dilute system of almost disconnected droplets, decorated with polymer loops. The latter observation stems from the fact that the average fraction of the looped polymers $\bar{\lambda}$, is given by:

$$\bar{\lambda} = -\frac{\partial \ln(Z_1)}{\partial \epsilon} = \frac{\frac{q_l}{q}e^{-\epsilon}}{\frac{q_l}{q}e^{-\epsilon} + c} \quad (4)$$

as follows from eq.(1). Thus, the fraction of looped polymers $\bar{\lambda}$ tends to unity in the dilute phase, where $c \ll \frac{q_l}{q}e^{-\epsilon}$. From the equality of the polymer chemical potential, $\mu_\phi = \ln \frac{\phi}{qc^2 + q_l e^{-\epsilon} c}$ in the coexisting phases, it follows that the phases that coexist lie along the lines $r = m(c + \frac{q_l}{q}e^{-\epsilon})$ in the (c, r) plane; where m is a constant determined by μ_ϕ , $m = e^{\mu_\phi}/q$. For any given $m > 4$, this line intersects the spinodal (eq. 3) at two points, as shown in Fig. 2. For $m = 4$ there is only one solution $\left(\frac{1}{2}, 2\left(1 + \frac{q_l}{2q}e^{-\epsilon}\right)\right)$ and the tie line is tangent to the spinodal; this determines the location of the critical point which in our mean field model is given by $c = 0.5$ independent of the value of the control parameter $\frac{q_l}{q}e^{-\epsilon}$, and the critical polymer to bead ratio, $r_c = 2\left(1 + \frac{q_l}{2q}e^{-\epsilon}\right)$. For $m < 4$ there is no phase coexistence. The predicted phase diagram of the system is shown in Fig. 2. Comparing the phase diagram of Fig. 2 with the experimentally observed one of Ref. [21]

We now estimate the parameter ϵ that reflects the reduction in the entropy of a polymer due to the constraint that both ends reside in the same droplet. In a simple approximation, the number of configurations available to a polymer with radius R_G , with both ends constrained to a volume v , that is small relative to the total volume available, is proportional to $\frac{v}{R_G^3} \simeq \frac{R_0^2 l}{R_G^3}$ where l is the length of the hydrophobic sticker. Therefore $e^{-\epsilon} \simeq \frac{R_0^2 l}{R_G^3}$ for $R_0 < R_G$ and saturates to unity for $R_0 > R_G$. The parameters q_l , q and ϵ (which is entropic in origin), combine to yield the single control parameter of the system: $q_l e^{-\epsilon}/q$. Using typical values of the droplet radius, polymers radius of gyration and the size of the hydrophobic stickers from Ref.[21], we estimate the control parameter $q_l e^{-\epsilon}/q \sim 2 - 3$.

It is important to realize that the predicted phase separation *cannot* be attributed to the direct attraction between the beads induced by the connecting polymers; the total polymer stretching energy site is $E \simeq \frac{1}{2}\phi \int \frac{E_R e^{-E_R/T} q_R dR}{e^{-E_R/T} q_R dR}$ and is irrelevant for the phase separation because it is linear in polymer density ϕ .

Due to its entropic nature, the phase separation is extremely robust and is independent of the detailed assumptions about the polymer properties. It persists even

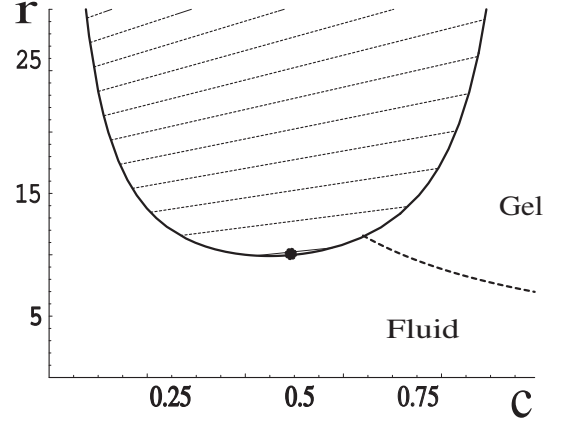


FIG. 2: Phase diagram of drops connected with polymers. The thick line is the spinodal line of the phase separation for $q_l e^{-\epsilon}/q = 2$. Above this line the system becomes thermodynamically unstable. The critical point is at $c = 0.5$ and is shown as a black dot. Note that the critical point is *not* at the minimum of the spinodal. The tie-lines are shown as dotted lines in the phase separation region. Note that they are *not* horizontal. The dashed line shows the percolation threshold calculated for an f.c.c. lattice with $q = 16$. Below the percolation line, the system is in the fluid state, while above it a connected gel is formed. One should remember that the experimentally controlled volume fraction of the beads is equal to $c \frac{R_0^3}{(R_G + R_0)^3}$

in the limit of very short and rigid chains, that connect only nearest neighbor drops, complementary to the case of flexible chains discussed above. Neglecting the single bead loops (which can be shown to be unimportant in this limit), the total number of ways to distribute N_p indistinguishable polymers among $P \equiv \frac{1}{2}qcN$ nearest neighbor pairs is $\frac{(N_p + P - 1)!}{N_p! (P - 1)!}$ [27] and the total free energy per unit volume is $f \simeq -S_0(c) + \frac{1}{2}qc^2 (\ln(\frac{1}{2}qc^2) - 1) - \frac{1}{2}qc^2 \ln \phi$ when $r = 2\phi/c \gg 1$. This free energy also exhibits a phase separation between a dense, highly connected phase in equilibrium with a dilute solution of beads.

The mean field picture can be improved by using an *exact* mapping of the droplet-polymer system to a lattice gas model. Denoting the chemical potential of the beads as μ_b and that of the polymers as μ_p , the grand canonical partition function of the polymer-microemulsion system (with no loops) can be written as

$$\begin{aligned} \Theta &= \sum_{N,P} \Omega(N,P) \sum_{N_p=0}^{\infty} \frac{(N_p + P - 1)!}{N_p! (P - 1)!} e^{\mu_b N + \mu_p N_p} \\ &= \sum_{N,P} \Omega(N,P) e^{\mu_b N} (1 - e^{\mu_p})^{-P} \end{aligned} \quad (5)$$

here $\Omega(N,P)$ is the number of ways to arrange N drops so that P nearest neighbor pairs of drops exist in a *given* realization of the grand canonical ensemble (P is equal to $\frac{1}{2}cN$ only in the mean field approximation).

Eq. (5) *exactly* corresponds to the grand canonical partition function of a lattice-gas with a Hamiltonian $H = \ln(1 - e^{\mu_p}) \sum_{\langle i,j \rangle} \sigma_i \sigma_j + \mu_b \sum_i \sigma_i$. Thus, the polymer chemical potential μ_p , related to the number of the polymers in the system, plays the role of the interaction parameter that controls the phase separation. Note that this mapping can be extended off-lattice using similar, although more complicated, arguments. The very general nature of this mapping pertains to any system of linked beads, and the results described in this Letter apply to many different experimental realizations, including DNA nanoparticles assemblies [7] and antigen-antibodies immunoassays [1].

Percolation: The transition from a fluid-like state to an elastic gel is related to the formation of an infinite network of droplets connected by polymers. This is described by site-bond percolation models that have been applied to study gelation [16]. The vertices of a lattice are occupied with probability p_s , and a bond can form between two, occupied, nearest neighbors with probability p_b . Percolation is said to occur when an infinite cluster of occupied sites, connected by the bonds, is formed. In our system, the site-occupation probability p_s can be identified with the droplet concentration, c . The "bond occupation" probability can be identified as the probability that at least one polymer connects a given pair of beads. For a given numbers of chain ends per droplet, r , the average number of bonding polymers per available nearest neighbor pair of drops is $r_b = \frac{r(1-\bar{\lambda})}{q_c}$ where $\bar{\lambda}$ is the average fraction of looped polymers, Eq.(4). To a good approximation, the probability p_n that a given pair of nearest neighbor droplets is connected by n polymers, obeys the Poisson distribution, $p_n = \frac{r_b^n}{n!} e^{-r_b}$. Thus, bond probability is $p_b = \sum_{n=1}^{\infty} p_n = 1 - e^{-r_b}$. Previous studies of percolation have shown [24] that the percolation line in the (p_b, p_s) plane follows a power law $p_b = (p_s)^\alpha p_b^c$ where

$\alpha = -\frac{\ln p_b^c}{\ln p_s^c}$ and p_b^c and p_s^c are the percolation thresholds for independently calculated bond and site percolation on the given lattice. Although lattice models for percolation cannot be applied in a quantitative manner to the continuum, polymer-droplet system they provide a qualitative indication of the gelation transition as shown in Fig. 2.

Simulations: To independently verify the predictions of the analytical model, we have performed the Monte Carlo simulations in the grand-canonical ensemble of both beads and polymers, with chemical potentials μ_b and μ_p , respectively. The simulated phase behavior also exhibits a first order transition between a dense connected network and a dilute phase. The detailed results of the simulations will be presented elsewhere [28].

The predicted phase diagram, summarized in Fig. 2, reproduces the experimentally observed phase behavior of the model transient network of Ref.[21], shown in Fig. 1 a). The spatial phase separation described in this Letter originates from a purely entropic effect, observed in other physical systems as well [22, 23]. Namely, the loss of entropy due to spatial inhomogeneity and formation of the dense phase, is overcompensated by the increase in the polymer configurations. The simplicity of the experimental realization which allows for easy control over the system parameters, the described system can be extended to cover a wide range of equilibrium and non-equilibrium networks, in particular to examine the role of entropic effects in the formation of spatially inhomogeneous structures in non-equilibrium networks[25, 26]. The authors thank D. Lukatsky for a critical reading of the manuscript and N. Gov, J.F. Joanny, S. Havlin and A. Rotem for helpful comments. The support from GIF foundation and the PRF fund, administered by the American Chemical Society, is gratefully acknowledged.

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